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By: *Mary C. Notter*
Name: Mary C. Notter

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REQUEST FOR PROVISIONAL APPLICATION UNDER 37 C.F.R. § 1.53(c)

MAIL STOP PROVISIONAL PATENT APPLICATION

Commissioner for Patents
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Dear Sir:

This is a request for filing a Provisional application for patent under 37 CFR § 1.53(c) entitled NOVEL PHOTOPOLYMERS AND USE IN DENTAL RESTORATIVE MATERIALS by the following inventor(s):

| | | | |
|-------------------------|---------------------------------------------------------|---------------------------------|-----------------------------------------|
| Full Name Of Inventor | Family Name Bowman | First Given Name Christopher | Second Given Name N. |
| Residence & Citizenship | City Boulder | State or Foreign Country CO | Country of Citizenship US |
| Post Office Address | Post Office Address 3212 47th Street | City Boulder | State & Zip Code/Country CO 80301/US |
| Full Name Of Inventor | Family Name Lu | First Given Name Hui | Second Given Name |
| Residence & Citizenship | City Boulder | State or Foreign Country CO | Country of Citizenship PR China |
| Post Office Address | Post Office Address 2980 E. Euclid Avenue, Apt. A-17 | City Boulder | State & Zip Code/Country CO 80303/US |
| Full Name Of Inventor | Family Name Stansbury | First Given Name Jeffrey | Second Given Name W. |
| Residence & Citizenship | City Aurora | State or Foreign Country CO | Country of Citizenship US |
| Post Office Address | Post Office Address 18111 East Ida Place | City Aurora | State & Zip Code/Country CO 80015/US |

- ☒ Enclosed is the Provisional application for patent as follows: 12 pages of specification
- ☐ Small entity status is claimed pursuant to 37 CFR 1.27.
- ☒ Payment of Provisional filing fee under 37 C.F.R. § 1.16(k) :
 - ☒ Attached is a check in the amount of \$ 160.00.
 - ☐ Please charge Deposit Account No. 13-2725.
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8. ☒ Address all future communications to the Attention of George C. Lewis (may only be completed by attorney or agent of record) at the address below.
9. ☒ A return postcard is enclosed.

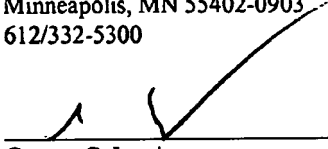
Respectfully submitted,

MERCHANT & GOULD P.C.
P.O. Box 2903
Minneapolis, MN 55402-0903
612/332-5300



Date: _____

10/22/03



George C. Lewis
Reg. No. 53,214
GCLewis/mcn

PROVISIONAL PATENT APPLICATION

**NOVEL PHOTOPOLYMERS AND USE IN DENTAL
RESTORATIVE MATERIALS**

INVENTORS:

Christopher N. Bowman

Hui Lu

Jeffrey W. Stansbury

FIELD OF THE INVENTION

The present invention relates to a thiol-ene polymer system with high conversion and more particularly to a thiol-ene polymer system for use as a dental restorative resin.

BACKGROUND

Currently, commercial photoactivated dental restorative resins are based on dimethacrylates and the reaction mechanism is through chain-growth free radical polymerization. Existing dimethacrylate systems are popular for fillings and other dental prostheses because of their esthetic merit and "cure-on-command" feature.

Such dental restorative materials are often mixed with 45 to 85 wt% silanized filler compounds such as barium, strontium, zirconia silicate and/or amorphous silica to match the color and opacity to a particular use or tooth. The filler is typically in the form of particles with a size ranging from 0.01 to 5.0 micrometers.

The photoactivated restorative materials are often sold in separate syringes or single-dose capsules of different shades. If provided in a syringe, the user dispenses (by pressing a plunger or turning a screw adapted plunger on the syringe) the necessary amount of restorative material from the syringe onto a suitable mixing surface. Then the material is placed directly into the cavity, mold, or location of use. If provided as a single-dose capsule, the capsule is placed into a dispensing device that can dispense the material directly into the cavity, mold, etc. After the restorative material is placed, it is photopolymerized or cured by exposing the restorative material to the appropriate light source. The resulting cured polymer may then be finished or polished as necessary with appropriate tools. Such dental restoratives can be used for direct anterior and posterior restorations, core build-ups, splinting and indirect restorations including inlays, onlays and veneers.

Although easy to use, these systems have several drawbacks, primarily associated with the polymerization volume shrinkage and shrinkage stress, and poor conversion of the dimethacrylate systems' monomers into polymer. The current systems can only reach a final double bond conversion of 55 to 75 %, which not only contributes to the insufficient wear resistance and mechanical properties, but also jeopardizes the biocompatibility of the composites due to the leachable unreacted monomers. Dimethacrylate based resins exhibit significant volumetric shrinkage during polymerization and the induced shrinkage stress results in tooth-composite adhesive failure, initiating microleakage and recurrent caries, which significantly reduces the longevity and utility of current dental restorative composite. Furthermore, as one tries to increase the final double bond conversion to reduce the unreacted monomers, the volumetric shrinkage and shrinkage stress unfortunately also increase, which has been a persisting problem since the development of this class of resins.

WRITTEN DESCRIPTION OF INVENTION

The present invention can be thought of as a thiol-ene system with a high conversion, low shrinkage and low odor during curing. A thiol-ene system having

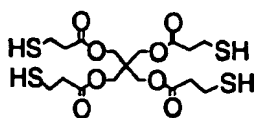
15%-60% by weight of its functional groups as thiol functional groups is disclosed. The balance of the functional groups in the system can be vinyl groups. The vinyl groups may be provided by vinyl ethers, acrylates or other monomers containing vinyl groups. In addition to thiols and vinyl groups, additional functional groups may be provided to tailor and provide additional properties.

Thiol-ene systems may also include and/or utilize various initiators, fillers, and accelerators depending on the application. For example, if photopolymerization using visible light is desired, camphorquinone may be used as an initiator. Alternatively, if ultraviolet photopolymerization is desired, then 2,2-dimethoxy-2-phenylacetophenone (DMPA) may be used as an initiator. Amine accelerators may also be used, as well as other accelerators. However, we have found that thiol-ene system can be readily initiated by just camphorquinone, without the presence of the amine accelerator. This is largely beneficial to the biocompatibility of photo-cured dental composites since studies have shown that certain tertiary amine accelerators, such as N,N-dimethyl-p-toluidine, are carcinogenic and mutagenic.

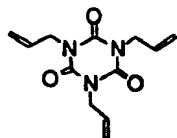
The thiol-ene systems of the present invention have some significant and unique advantages compared with (meth)acrylate polymerizations, which are extremely beneficial for dental resin applications. These advantages include: high gel-point conversion which will significantly decrease shrinkage stress; rapid polymerization rate and lack of oxygen inhibition; nearly complete consumption of low molecular weight reacting species due to the nature of the step-growth mechanism, which limits the amount of leachable species and exhibiting less perceptible odor; versatile kinetics and structure-property design based on tailoring the thiol-ene monomer chemistry.

Another advantage of thiol-ene systems is that they can replace existing methacrylate systems. Thiol-ene polymers can be mixed and applied in the same manner currently used by dentists using methacrylate systems. The thiol-ene systems can be mixed with fillers as is typical in methacrylate systems. Depending on the initiator used, existing light sources used to photopolymerize the methacrylate systems may also be used. Likewise, dental restorative materials using thiol-ene polymer systems may be supplied in single-dose capsules or syringes.

Our work on the thiol-ene polymers as dental restorative materials has revolved around the demonstration of the feasibility and advantages of these polymers over currently used dental restorative materials. More specifically, the following monomers were studied:



Pentaerythritol tetramercaptopropionate (PETMP)



Triallyl-1,3,5-triazine-2,4,6-trione (TATATO)



1-Octanethiol



1,6-Hexanedithiol

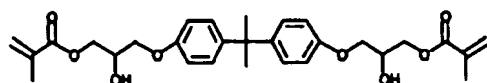


Triethyleneglycol divinyl ether (TEGDVE)

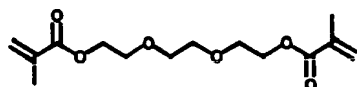


Dodecyl Vinyl ether (DDVE)

In addition, the following methacrylate system was used as a comparison:

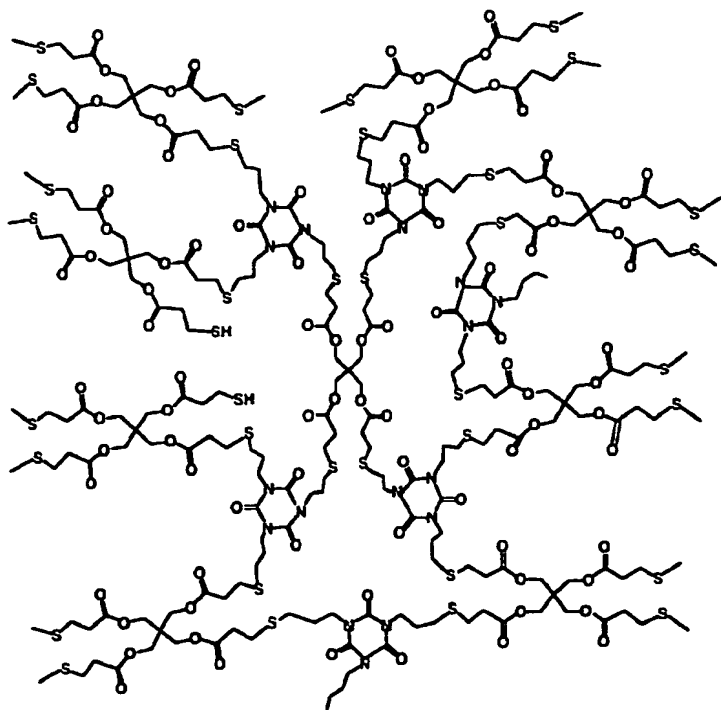


2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropyloxy) phenyl] propane (Bis-GMA)



Triethyleneglycol dimethacrylate (TEGDMA)

The various systems above were polymerized under various conditions and the resulting polymers were tested. The following is a representation of a thiol-ene polymer created using PETMP/TATAO.



Polymerization kinetics investigation of thiol-ene systems

FTIR (Magna 750, Nicolet Instrument Corp., Madison, WI) was used to study the polymerization kinetics of the thiol-ene materials used in this study because of its inherent advantage of being able to measure the thiol and vinyl conversions simultaneously and rapidly. The infrared peak at 1643 cm^{-1} was used for determining the allyl group conversion (of TATATO) and the peak at 2572 cm^{-1} was used for the thiol group conversion. As shown in Figure 1, the polymerization of PETMP/TATATO occurs at a much higher rate than the typical dental restorative resin system Bis-GMA/TEGDMA (70/30 by wt.) cured under the same conditions. The final conversion of the allyl was found to be 90% while the thiol final conversion was 86%, while for Bis-GMA/TEGDMA the final conversion is only about 65%. The slight difference in the final conversion of the allyl and the thiol is caused by a small amount of homopolymerization that occurs with the allyl functional group. In addition to the PETMP/TATATO system, a vinyl ether oligomer was copolymerized with the PETMP to evaluate the relative performance of vinyl ether. VEctomer® VE1312 (Morflex Inc., Greensboro, NC) is a multifunctional vinyl ether containing a multifunctional polyester backbone. Its number average molecular weight is 1250 g/mol, with average functionality of 3.4. Clearly, the combination of oligomerizing the vinyl group and changing to the vinyl ether increased the polymerization rate significantly. For all of the commercial systems studied containing multithiols and multivinyls of either allyls, allyl ethers or vinyl ethers, the polymerizations all achieved much higher conversions and reacted much more quickly to that conversion. In addition, dramatically reduced oxygen inhibition has been observed for all the thiol-ene polymerizations, as shown in Figure 1. Also note that ultraviolet light was used for all of the preliminary studies to simplify the initiating system though we have also demonstrated that camphorquinone by itself readily initiates these polymerizations without the presence of the amine accelerator.

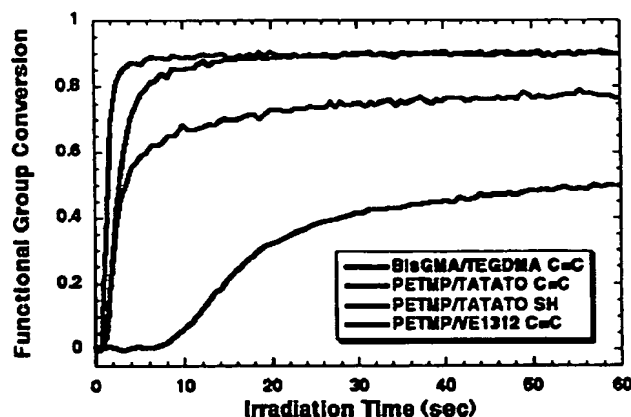


Figure 1. Conversion of allyl and thiol functional groups of PETMP/TATATO, the vinyl group of PETMP/VE1312, and Bis-GMA/TEGDMA (70/30 by wt.) as a function of irradiation time; 0.1wt% DMPA; UV=5.0 mW/cm²; T_{cure}= 37°C. All thiol-ene monomer mixtures were prepared to have an equivalent concentration of the two functional groups.

Material properties investigation of commercial thiol-ene systems

In addition to the kinetics, various material property measurements were performed. Specimens for dynamic mechanical analysis (DMA) testing were photocured for 10 min with 10.0 mW/cm² of UV light at ambient conditions. A DMA7e (Perkin-Elmer, Norwalk, CT) was used to measure the glass transition temperature, T_g , of poly (PETMP/TATATO). DMA was conducted over a temperature range of -50 ~ 120 °C with a ramping rate of 5 °C using extension mode (sinusoidal stress of 1 Hz frequency) and the tan δ peak was monitored as a function of temperature as shown in Figure 2. For this sample, the glass transition temperature was found to be 64°C. Each sample for the property measurement was prepared with an equal molar ratio of thiol functional groups to vinyl functional groups and was monitored with near infrared spectroscopy. Under these conditions, the vinyl group conversion was found to be approximately 90% in all cases.

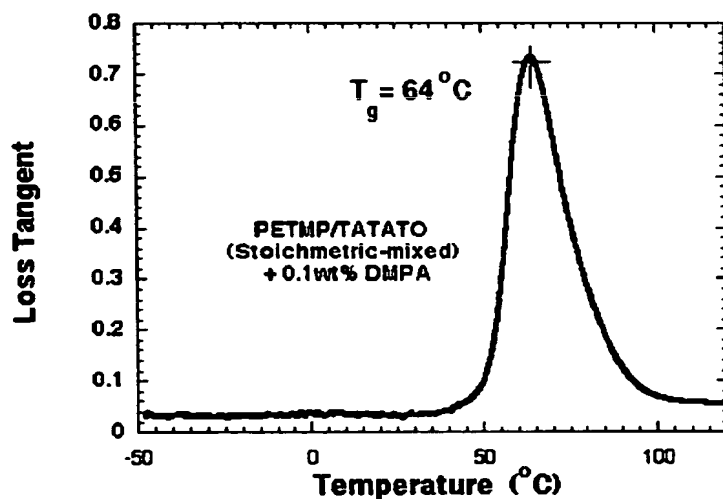


Figure 2. Loss tangent as a function of temperature for PETMP/TATATO (Molar ratio: 3:4) polymer.

For the flexural strength studies, monomer samples were photopolymerized in a Teflon[®] mold (specimen dimensions: 25±2 mm × 2±0.1 mm × 2±0.1 mm) with 10.0 mW/cm² of UV light for 10 min at ambient conditions. Four specimens were prepared for each sample. A 3-point flexural test was carried out with a MTS[®] 858 Mini Bioix system (MTS Systems Corporation, Eden Prairie, MN, USA) using a span width of 20 mm (10 mm for PETMP/TATATO) and a crosshead speed of 1 mm/min. The flexural strength (σ) and flexural modulus (E_f) were calculated using the following equations:

$$\sigma = \frac{3Fl}{2bh^2} \quad (1)$$

$$E_f = \frac{F_1 l^3}{4bh^3 d} \quad (2)$$

where F is the peak load (in N), l is the span length (in mm), b is the specimen width (in mm), h is the specimen thickness (in mm); and d is the deflection (in mm) at load F_1

(in N) during the straight line portion of the trace (ISO/DIS 4049, 1987). The results from this study show that the mechanical properties of the current formulation are not as high as the current Bis-GMA/TEGDMA resin system. This issue is largely what drives the need for new thiol and ene monomers that have a lower equivalent weight (larger number of functional groups for the same molecular weight monomer), to be oligomerized, and contain more rigid cores that will improve the resin modulus and strength.

Table 1. Flexural strength test results for PETMP/TATATO and Bis-GMA/TEGDMA

| System | σ (MPa) | E_r (MPa) | Strain at Break (%) |
|-----------------------------------|----------------|----------------|---------------------|
| PETMP/TATATO (Molar Ratio 3:4) | 67 \pm 4 | 1300 \pm 100 | 11 \pm 1 |
| Bis-GMA/TEGDMA (Mass Ratio 70:30) | 93 \pm 5 | 2300 \pm 80 | 7 \pm 2 |

In addition to measuring the flexural strength and glass transition temperature of the model thiol-ene system, extraction studies were performed. As per Stansbury et al. each specimen was weighed immediately following polymerization. Soxhlet extraction of each specimen was conducted for 10 hours at 60°C, with dichloromethane used as the solvent. The mid-IR spectrum of the solvent after extraction was obtained and compared with that of the pure dichloromethane. No change in the infrared spectrum of the extracting dichloromethane was observed when compared with the pure dichloromethane. Also, no detectable substance was found following rotary evaporation of the extracting dichloromethane. After extraction, each specimen was dried to constant mass under 20 inch Hg vacuum at 60°C. For the thiol-ene samples this process took approximately 60 hours, and the average weight loss of the dried specimens was found to be 0.5% \pm 0.1% relative to the original mass before extraction. This number compares extremely well with 11% extraction loss in a typical Bis-GMA/TEGDMA control sample polymerized under similar conditions to 68% methacrylate conversion. The number also compares reasonably well with the prediction for the amount of unreacted monomer remaining in the system, i.e., the amount of thiol or ene monomer that has not one of its functional groups reacted. Using the 86% thiol conversion and 90% vinyl conversion, the fraction of thiol monomer unreacted is (for the tetrathiol monomer) $(1-0.86)^4 = 0.04\%$ and the fraction of unreacted vinyl monomer is (for the trivinyl monomer) $(1-0.9)^3 = 0.1\%$. Thus, it is not expected that there would be a significant amount of extractable material at these conversions.

Finally, to demonstrate physically some of the advantages of thiol-ene polymers, large, stress-free samples were prepared by photopolymerization of thiol-ene systems. These polymers include a 20 inch long rod that was polymerized from the top and a solid ball that was also polymerized from the top. The ball is approximately two inches in diameter. Each of these materials had minimal shrinkage, and more importantly, remained uncracked throughout the polymerization due to the minimal polymerization shrinkage stress. These samples are presented in Figure 3 below.



Figure 3. Picture of thiol-ene polymeric ball and rod

Polymerization volume shrinkage of thiol-ene polymers

For samples such as many of the thiol-ene polymerizations that are lower viscosity and have relatively high gel point conversions, it is necessary to develop a different methodology for volume shrinkage measurements. For these systems, a straightforward method to measure the volume shrinkage was applied: measure the initial volume before polymerization by measuring the long dimension in a narrow, constant diameter tube, photo-cure the monomer, and then measure the final volume after polymerization by measuring the long dimension again. This technique is especially useful in studying the shrinkage of the stepwise-polymerized linear or crosslinking system, the latter has a much delayed gel-point and is therefore inappropriate to study using linometer or strain gauge. By using this approach, we have investigated the volume shrinkage of Thiol-vinyl ether and thiol-(triallyl-triazine-trione) systems, which hasn't been systematically studied before. Interestingly, the molar volume change for C=C during polymerization are much lower than the acrylate or methacrylate systems, which produce 22.5~23 ml of shrinkage for every mole of double bond polymerized. Table 2 showed the results of this volume shrinkage study. Thus, it is not only the dramatic increase in gel point conversion that will reduce the shrinkage stress in this system, but also the fact that each double bonds that reacts leads to approximately half of the shrinkage that occurs in a traditional free radical polymerization.

Table 2. Volume shrinkage measurement using static volume change method

| System | Volume Shrinkage (%) | Molar Volume Change for C=C (ml/mol) |
|-------------------------------|----------------------|--------------------------------------|
| MMA (Patel et al. 1983) | 20.6 | 22.5 |
| HDT/TEGDVE (Molar Ratio: 1:1) | 7.1 | 12.7 |
| OT/DDVE (Molar Ratio: 1:1) | 2.9 | 12.6 |
| OT/TATATO (Molar Ratio: 3:1) | 6.1 | 15.1 |

MMA: Methyl methacrylate; HDT:1,6-Hexanedithiol; TEGDVE: Triethylene glycol di(vinyl ether); OT:1-Octanedithiol; DDVE: Dodecyl vinyl ether; TATATO: Triallyl-1,3,5-triazine-2,4,6-trione.

Simultaneous measurement of thiol-ene shrinkage stress and conversion

This experimental set-up is capable of simultaneous measurement of the shrinkage stress and conversion, both on exactly the same sample at the same time. The *in situ*, real-time monitoring of the polymerization was achieved by guiding the near-IR beam through the sample, which was mounted on the tensometer, then refocusing the transmitted signal to the near-IR detector. The tensometer, designed by American Dental Association (ADA), is based on the cantilever beam deflection theory: shrinkage force generated by the composite during curing causes the beam to bend, and the deflection is measured with a linear variable differential transformer (LVDT). The shrinkage force is then calculated using the beam constant of the cantilever beam. Therefore, the shrinkage stress value is obtained by dividing the shrinkage force by the composite sample cross-sectional area. With the combination of different beam lengths and materials, it is possible to measure the shrinkage stress accurately over a wide range of values. Figure 4 below presents a picture of this novel experiment set-up.

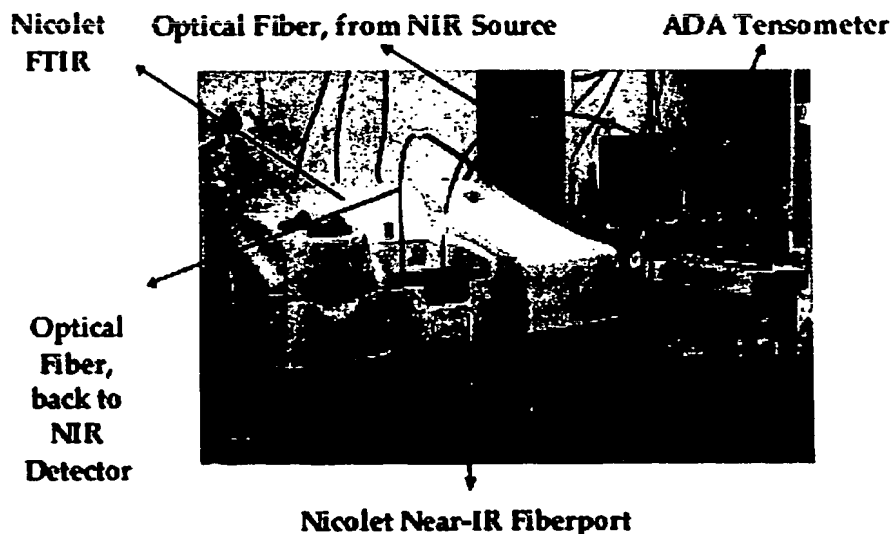


Figure 4. Picture of simultaneous shrinkage stress and conversion measurement setup

Using the combined tensometer and remote near-IR technique, the simultaneous shrinkage stress and conversion of Bis-GMA/TEGDMA and PEPMP/TATATO were measured from the same sample at the same time. As shown in Figure 5, the final shrinkage stress achieved by PETMP/TATATO system is less than 12% of the Bis-GMA/TEGDMA system, both cured under identical conditions. The extremely low shrinkage stress of thiol-ene polymers resulted from not only the relatively high gel point conversion but reduced volume shrinkage that each double bond generates during polymerization. The shrinkage stress as a function of double bond conversion was shown in Figure 6. It further illustrated the advantages of thiol-ene polymers for dental restorative materials: dramatically reduced shrinkage stress and improved functional group conversion.

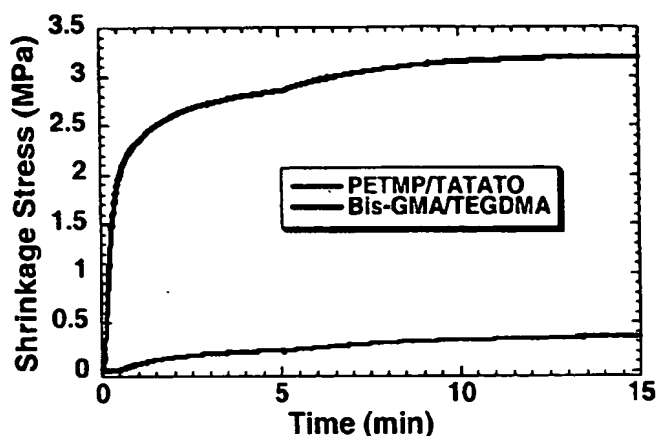


Figure 5. Shrinkage stress as a function of time of Bis-GMA/TEGDMA and PETMP/TATATO, cured with visible light at 330 mW/cm^2 for 5 min at room temperature

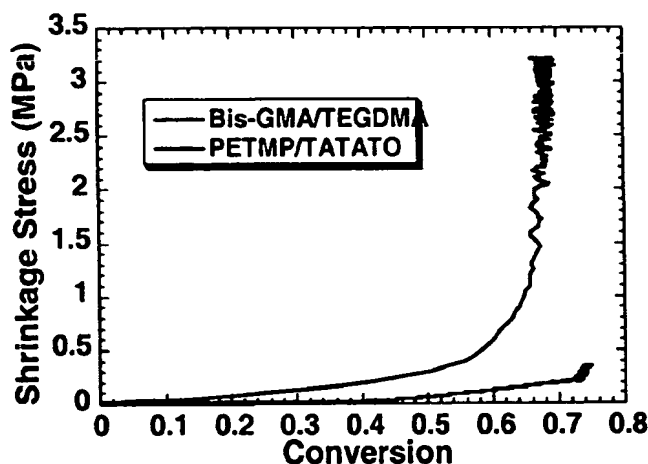


Figure 6. Shrinkage stress as a function of double bond conversion of Bis-GMA/TEGDMA and PETMP/TATATO, cured with visible light at 330 mW/cm^2 for 5 min at room temperature

Synthesis of reactive oligomeric thiol and ene materials

The purposes of synthesizing oligomeric thiol and ene materials are to optimize both polymer properties and polymerization performance and eliminate odor concerns. Because of the step growth nature of the thiol-ene photopolymerization, it is possible to oligomerize (both synthetic and commercially available) monomers to a significantly higher extent of polymerization prior to formulating the materials and completing the polymerization in the restoration. This technique will have enormous advantages over current thiol-ene systems that are low molecular weight. First, since the overall functional group concentration will be decreased dramatically, the shrinkage will correspondingly be decreased while still maintaining the identical ultimate network structure and material properties. Secondly, with higher molecular weight thiols, it will be more facile to purify the oligomers and remove the trace, low molecular weight compounds responsible for the odor in these systems and to limit further the amount of extractables.

Commercial dental restorative resins are based on dimethacrylates and the reaction mechanism is through chain-growth free radical polymerization. The thiol-ene

polymerization proceeds through a totally different route: step growth polymerization facilitated by rapid and facile chain transfer. Besides the impact of the polymerization mechanism on the gel point conversion and network formation, the thiol-ene systems have demonstrated decreased volume shrinkage and shrinkage stress during polymerization. In summary, the uniqueness of this invention is:

- Thiol-ene polymerization has demonstrated dramatically reduced volume shrinkage, which hasn't been reported previously in the literature.
- Thiol-ene polymerizations have a significantly increased gel point conversion, which, together with the low shrinkage, results in ultra-low shrinkage stress. This feature is extremely beneficial to the dental restorative composite applications, which cannot be achieved by any current free radically polymerized dental resin systems.
- The oligomerization of thiol-ene monomers will further reduce the polymerization shrinkage. In addition, elimination of low molecular weight reactants during oligomerization will result in dental resins with less odor than current methacrylate based systems.
- Due to the mechanisms of the thiol-ene polymerization and the high conversion that has been achieved in the preliminary experiments, thiol-ene polymers contain much less unreacted monomer that can be leached out into the oral environment. This has been confirmed with the solvent extraction experiments conducted on commercial thiol-ene systems.
- The thiol-ene polymerization has demonstrated much thicker curing depth than methacrylate based resin systems. This will greatly reduce the patient's chair-time since one-step curing is feasible, especially for large cavity filling, where incremental filling has to be applied using current dental composite systems.
- Reduced volume shrinkage during polymerization and the dramatically reduced shrinkage stress due to the reduced volume shrinkage and significantly delayed gel point conversion. These features will greatly alleviate the problems associated with shrinkage stress from current resin systems, such as interfacial bonding failure, microleakage and recurrent caries.
- The extremely high functional group conversion of thiol-ene polymers significantly mitigates the problems associated with the current dimethacrylate resin systems which is associated with the incomplete double bond conversion.
- The thick cure depth and lack of oxygen inhibition of thiol-ene systems leads to one-step filling and curing during restorations, compared with the incremental filling technique using current dental resin systems.
- The thiol-ene systems can be initiated by camphorquinone itself under visible light irradiation, without the presence of the amine accelerator.

CONCLUSION

Composite resin materials are widely used not only for filling cavities, but also for reconstructing dental structures, luting restorations and orthodontic applications. Thiol-ene polymers have great potential to replace the current dental composite systems based on dimethacrylate resins, as demonstrated in our preliminary studies. The numerous advantages of the thiol-ene systems will dramatically increase the life-time of dental restorative composites. Companies which manufacture dental restorative composites will find this invention enormously useful and beneficial. In the long run, tens of millions of patients who require dental restorations will be the ultimate beneficiaries of the thiol-ene dental restoration systems. Therefore, we believe those companies in the dental cure and biomedical fields will show great interest in this invention.

Investigation of Thiol-Ene System for Novel Dental Restorative Resins

Bowman, CN^{1,2}, Lu, H¹, Stansbury, JW^{1,2}, Cramer, NB¹

¹ University of Colorado, Boulder, CO, USA

² University of Colorado Health Sciences Center, Denver, CO, USA

Introduction

Although it has been commercialized for 40 years, restorative dental resin formulas based on dimethacrylate have barely changed. The fundamental drawbacks associated with this class of chain-growth polymerized system, such as volumetric shrinkage, shrinkage stress, and incomplete final conversion, are only mitigated through optimizing with filler and bonding systems. However, none of these problems can be fully eliminated due to the nature of this class of materials and the polymerization mechanism. Therefore, non-acrylate type monomer systems and polymerization mechanisms are being actively investigated as alternative dental resins.

Chain-growth polymerized dimethacrylate resins have very low gel point conversions, which contribute to the high shrinkage stress feature. Therefore, the opportunity to use a high-gel-point system such as the step-growth polymerized thiol-ene system as dental resins is investigated. Thiol-ene polymerizations have some significant and unique advantages compared with (meth)acrylate polymerizations, which are extremely beneficial for dental resin applications. These advantages include: high gel-point conversion which will significantly decrease shrinkage stress; rapid polymerization rate and lack of oxygen inhibition; nearly complete consumption of low molecular weight reacting species due to the nature of the step-growth mechanism, which limits the amount of leachable species; versatile kinetics and structure-property design based on tailoring the thiol-ene monomer chemistry.

In this study, we focused on demonstrating the feasibility of using crosslinked thiol-ene systems for dental restorative materials. Particularly, the shrinkage stress and conversion of the model thiol-ene system have been studied using the simultaneous shrinkage stress-conversion measurement set-up.

Materials and Methods

The thiol-ene system used in this study is composed of a tri-allyl: triallyl-1,3,5-triazine-2,4,6-trione (TATATO), and a tetra-thiol: pentaerythritol tetra mercaptopropionate (PETMP), forming a mixture that has an equal molar ratio of thiol to vinyl functional groups. This system is compared with a typical dimethacrylate based dental resin system: 2,2 bis[4-(2-hydroxy-3-methacryloyloxy-propoxy)phenyl] propane (Bis-GMA)/ triethyleneglycol dimethacrylate (TEGDMA) (70/30 wt).

FTIR was used to study the polymerization kinetics of the thiol-ene materials used in this study. The absorption peak at 1643 cm^{-1} was used for determining the allyl functional group conversion and the peak at 2572 cm^{-1} was used for the thiol functional group conversion.

The simultaneous measurement of polymerization shrinkage stress and functional group conversion of PETMP/TATATO system was performed on our novel set-up. Dynamic mechanical analysis (DMA) was used to measure its T_g and storage modulus. The flexural strength of poly(PETMP/TATATO) was measured on a MTS. In addition, solvent extraction studies were performed with dichloromethane used as the solvent.

Results and Discussion

It was found that the polymerization of PETMP/TATATO occurs at a much higher rate than Bis-GMA/TEGDMA cured under the identical conditions. Moreover, the final conversion of the allyl was found to be 90% while the thiol final conversion was 86%, while for Bis-GMA/TEGDMA the final conversion is only about 65%. The slight difference in the final conversion of the allyl and the thiol is caused by a small amount of homopolymerization that occurs with the allyl functional group. In addition to the PETMP/TATATO system, vinyl ether oligomer was copolymerized with the PETMP to evaluate the relative performance of a vinyl ether. For all of the commercial systems studied containing multithiols and multivinyls of either allyls, allyl ethers or vinyl ethers, the polymerizations all achieved much higher conversions and reacted much more quickly to that conversion.

The simultaneous shrinkage stress as a function of double bond conversion is shown in Figure 1. It can be seen that shrinkage stress did not start to build up until approaching the gel point conversion (theoretical gel point $f_c = 40.8\%$ for this system). This agrees very well with the prediction that any volume shrinkage that occurred before the gel point will not result in shrinkage stress, as the shrinkage can be readily accommodated by the flow of the liquid mixture of oligomers. The maximum shrinkage stress developed was about 0.21 MPa, which was less than 10% of the maximum shrinkage stress of the Bis-GMA/TEGDMA system cured under the same conditions.

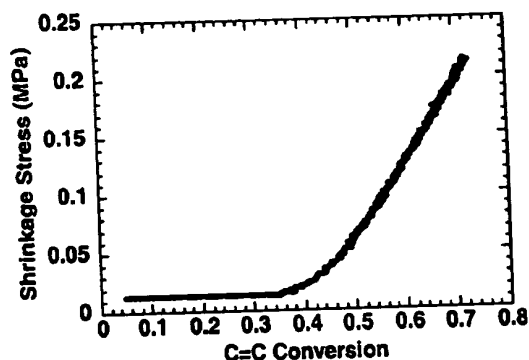


Figure 1. Simultaneous measurement of shrinkage stress as a function of conversion for PETMP/TATATO system (0.5 wt% CQ) cured using 375 mW/cm^2 visible light.

The T_g of PETMP/TATATO was found to be 64°C , close to the value of the current commercial resin system polymerized under similar conditions. In addition, the average weight loss of the dried specimens was found to be $0.5 \pm 0.1\%$ relative to the original mass before extraction, which is much lower than the extractable of Bis-GMA/TEGDMA control sample.

Conclusion

The dramatically reduced shrinkage stress, significantly increased functional group conversion, and decreased leachable species are all greatly beneficial for the use of thiol-ene systems as future dental restorative resins.

CLAIMS

We Claim:

1. A method of preparing a shaped dental prosthetic device for use in a human mouth comprising:
 - dispensing a mixture a first monomer and a second monomer, each first monomer having at least one thiol functional group and each second monomer having at least one vinyl functional group, wherein 15% to 60% of the functional groups in the monomer mixture are thiol groups;
 - shaping the monomer mixture; and
 - photopolymerizing the monomer mixture.
2. A dental prosthetic device comprising:
 - a polymer created from the polymerization of a first monomer having thiol functional groups and a second monomer having vinyl functional groups; wherein at least 15% the functional groups of the polymer are thiol functional groups.
3. A photopolymerizable dental restorative material comprising:
 - a filler;
 - a first monomer having thiol functional groups;
 - a second monomer having vinyl functional groups; and
 - an initiator;
 - wherein at least 15% of the functional groups in the dental restorative material are thiol functional groups.

ABSTRACT

Photopolymerizable polymer composites based on dimethacrylate systems have been increasingly utilized as dental restorative materials. One of the biggest drawbacks of current dental resin systems is the volume shrinkage and shrinkage induced stresses that arise during the polymerization. The volume shrinkage results from the conversion of methacrylate double bonds into single bonds. Other major problems include incomplete double bond conversion and insufficient wear resistance. This invention involves the development of an entirely novel approach to the photopolymerization process that utilizes thiol-ene systems as low shrinkage and ultra-low shrinkage stress dental restorative materials. Compared with the traditional dimethacrylate dental resins, these novel photopolymerizations have demonstrated a dramatically decreased volume shrinkage, extremely rapid polymerization, abilities to photopolymerize ultrathick materials and achieve much higher conversion, lack of oxygen inhibition and ultra-low shrinkage stress due to low volume shrinkage and drastically delayed gel point conversion. These polymers have thus shown outstanding promise in the application of dental restorative materials.

**Abstract for 82nd General Session of the International & American Association
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Novel Investigation of Thiol-Ene System for Future Dental Restorative Resins

**C.N. BOWMAN^{1,2}, H. LU¹, and J.W. STANSBURY^{1,2}, ¹University of Colorado,
Boulder, USA, ²University of Colorado Health Sciences Center, Denver, USA**

Objective: Non-acrylic monomer systems are being actively investigated as alternative dental resins due to the fundamental drawbacks associated with dimethacrylate-based resin systems. Thiol-ene polymerizations have dramatic and unique advantages compared with (meth)acrylate polymerizations. The feasibility of using crosslinked thiol-ene systems for dental restorative materials was investigated. **Methods:** The thiol-ene system investigated is composed of triallyl-1,3,5-triazine-2,4,6-trione (TATATO) and pentaerythritol tetramercaptopropionate (PETMP). The simultaneous measurement of polymerization shrinkage stress and functional group conversion of PETMP/TATATO system was performed. The samples' flexural strength, T_g and storage modulus were measured. Solvent extraction studies were performed. **Results:** The polymerization of PETMP/TATATO occurs at a much higher rate than Bis-GMA/TEGDMA cured under the identical conditions. Moreover, the allyl and thiol final conversions were found to be 90% and 86%, respectively (compared with 65% of Bis-GMA/TEGDMA control). The results from the simultaneous measurement of shrinkage stress and conversion showed that shrinkage stress did not start to build up until approaching the gel point conversion (theoretical gel point $f_c=40.8\%$ for this system). This agrees very well with the prediction that any volume shrinkage that occurred before the gel point will not result in shrinkage stress, as the shrinkage can be readily accommodated by the flow of the liquid mixture of oligomers. The maximum stress developed was about 0.21 MPa, less than 10% of the maximum shrinkage stress of the Bis-GMA/TEGDMA system cured under the same conditions. The average weight loss of the dried specimens was found to be $0.5 \pm 0.1\%$ relative to the original mass before extraction, which is much lower than the extractables from Bis-GMA/TEGDMA control samples. **Conclusions:** The dramatically reduced shrinkage stress, significantly increased functional group conversion, and decreased leachable species are all greatly beneficial for the use of thiol-ene systems as future dental restorative resins. (NIH grant# DE10959)

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